

PHASE DIAGRAM OF THE Ir-Sb SYSTEM ON THE ANTIMONY-RICH PART

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Abstract

The antimony-rich iridium antimony phase diagram was investigated by means of differential thermal analysis, microprobe analysis, metallography and X-ray powder diffraction. The existence of three compounds was confirmed in the range 50 to 100 at. % Sb: IrSb₃ which forms by peritectic reaction at 1141 °C, IrSb₂ which also forms peritectically at 1475 ± 30 °C and IrSb which melts congruently at 1645 ± 25 °C. IrSb₃ forms a degenerate eutectic with antimony at 621 °C. The shape of the liquidus line was also investigated.

Keywords: iridium, antimony, phase diagram

1. Introduction

The existence of the compound IrSb₃ was first reported in the literature by Zhuravlev

and Zhdanov [1]. A phase diagram of the Ir-Sb system in the range 50-100 (K) at.% Sb was previously established [2]. This determination was based on metallographic, thermal and X-ray analyses and the liquidus temperatures were determined from cooling curves. The melting temperature of the eutectic Sb - IrSb₃ was found to be 615°C and the eutectic composition was close to pure Sb. The existence of two compounds, IrSb₂ and IrSb₃, was established in this study. According to the same authors, the peritectic decomposition temperature of IrSb₃ was found to be between 800° and 950°C. However, the results of high temperature X-ray diffraction studies showed that no decomposition occurred up to 1000°C [3] and the authors concluded that the decomposition temperature must be between 1000 and 1200°C. The melting point of IrSb₂ is higher than 1050°C according to high temperature X-ray diffraction studies [4].

The compound IrSb₃ is cubic, isostructural with the skutterudite CoAs₃, and the lattice parameters can be found in references [1], [2], [3], [5], [6] and [7]. IrSb₂ is monoclinic with the CoSb₂ arsenopyrite structure and the lattice parameters can be found in references [4], [8] and [9]. Finally, the existence of a compound IrSb, isostructural with NiAs, was established by X-ray diffraction studies [10].

Transport properties measurements of samples prepared by the gradient freeze technique identified IrSb₃ as a new semiconductor which may be particularly interesting for thermoelectric applications [11]. The gradient freeze technique requires a good knowledge of the phase diagram. The phase diagram determined by Zhuravlev and Zhdanov [2] was used for the growth of the samples. It appeared that most of the samples prepared by this technique contained some antimony inclusions suggesting that the separation of the phases at the liquid-solid interface was not very efficient. This encouraged us to reinvestigate the Ir-Sb system in the range 50 to 100 at.% Sb.

2. Experimental details

Alloys in the composition range 50 to 100 at.% Sb were prepared for metallographic, Differential Thermal Analysis (DTA), X-Ray Diffractometry (XRD) and also optical and electron microprobe (MPA) investigations. The alloys were synthesized in quartz ampoules from stoichiometric amounts of high purity antimony (99.9999%) and iridium (99.95%). The ampoules were sealed under a vacuum of 10^{-5} Torr, heated in a resistance furnace at 1250°C for one day and then air-quenched. All the samples were subsequently annealed at a temperature of 550°C for 7 days.

A DuPont 1600 $^{\circ}\text{C}$ DTA apparatus was used for DTA measurements. The samples were sealed under 10^{-5} Torr vacuum in quartz capsules of 5 mm in diameter and 15 mm long. The rounded bottom of the capsule was flattened and thinned by grinding and fire polishing to provide a better thermal contact between the material and the thermocouple. Argon was used as the purge gas and heating and cooling rates were both $2^{\circ}\text{C}/\text{minute}$. The solid to liquid transformation temperatures were determined from the heating curves while the liquidus melting points were taken from the cooling curves. All the temperatures recorded by DTA were determined with an accuracy of $\pm 10^{\circ}\text{C}$. Because we used quartz capsules in order to prevent any antimony losses during the DTA experiments, the maximum recordable temperature was 1250°C . The melting point of samples higher than 1250°C were determined by direct observation of the samples after heating in a RF furnace. An optical pyrometer was used to control the furnace temperature and a calibration was done by melting standards of Ge, Si and Ni. Iridium antimonide samples were heated in thick wall quartz ampoules, cooled to room temperature and visually checked. If the sample had not melted, the procedure was repeated until the sample had melted completely. The uncertainty of this method was estimated at $\pm 25^{\circ}\text{C}$.

Microstructure of the samples, polished by standard metallographic techniques, were investigated using an optical Nikon microscope under both ordinary and polarized light. MPA analysis of selected samples was also performed on JEOL JXA-733 superprobe. X-ray diffraction analysis was conducted on some samples using a Siemens D-500 diffractometer with the $\text{Cu-K}\alpha$ radiation. Powder X-ray patterns were taken with steps scan of $2\theta = 0.05$ and counting time of 3 seconds.

3. Results and discussion

The results of the investigations are summarized in Figure 1 and table 1 gives the temperatures of the DTA results and also the results obtained by direct observation of the melting of the alloys.

All the DTA heating curves of alloys containing from 80 to 98.5 at. % Sb showed a thermal event at 621°C corresponding to the melting of the eutectic $\text{IrSb}_3 + \text{Sb}$ which has a composition very close to pure Sb suggesting that IrSb_3 forms a degenerate eutectic with antimony. The melting point of antimony (631.5°C) is lowered about 10°C by addition of iridium. Figure 2 illustrates the typical microstructure of the alloys in the range 80 to 98.5 at. % Sb after DTA. Two phases were detected by MPA and also XRD analyses in these alloys: IrSb_3 and Sb.

Alloys with 80, 91 and 95 at. % Sb were synthesized at 1250°C , held at this temperature for 30 minutes and then air-quenched. The typical microstructure of these alloys is shown on Figure 3. Two phases were detected by MPA in these alloys, i.e. antimony and the compound IrSb_2 . These results suggest that the compound IrSb_3 forms peritectically. Besides the thermal event at 621°C , alloys containing from 80 to 97 at. % Sb showed a second thermal event on the DTA heating curves at 1141°C corresponding

to the peritectic formation of the compound IrSb_3 . The boundary of the peritectic line was estimated at about 97 at. % Sb. MPA of the quenched alloys, subsequently annealed for 24 hours at 550 °C, showed that they contained also two phases but instead of IrSb_2 , the samples were formed of shaped IrSb_3 crystals inside an antimony matrix. Two phases were detected by MPA in an alloy containing 98.5 at. % Sb and quenched from a temperature of 1250 °C : IrSb_3 and antimony. The same two phases were also detected by MPA in a sample containing 95 at. % Sb and quenched from 1000°C.

MPA of an alloy containing 75 at. % Sb, synthesized at 1250°C and quenched, showed that it was composed of two phases: IrSb_2 and antimony. After annealing for ten days at 960°C, the sample was found to be single phase by MPA and its composition corresponded to the compound IrSb_3 . The DTA heating curve of this sample showed only one thermal arrest at 1144°C corresponding to the peritectic decomposition of the compound. The peritectic temperature of 1141 °C found in this study for the compound IrSb_3 is significantly higher than the one reported in reference [2] but is in agreement with the work of [3].

Figure 4 shows the microstructure of an alloy containing 57 at. % Sb synthesized at a temperature of about 1600°C and subsequently quenched. Large IrSb crystals can be seen within the IrSb_2 matrix. IrSb inclusions were also found in quenched samples up to a composition of 75 at. % Sb. These results indicate that the compound IrSb_2 forms peritectically. The peritectic temperature of IrSb_2 was estimated by determination of the different phases in the quenched alloys and was estimated at $1475 \pm 30^\circ\text{C}$. An alloy containing 66.66 at. % Sb, quenched from 1620 °C and subsequently annealed at 960°C for ten days, appeared to be single phase with a composition corresponding to the compound IrSb_2 . Melts containing 50 at. % Sb and quenched appeared to be single phase by MPA, indicating that IrSb melts congruently. The melting point was estimated at 1645

± 25 °C.

The Ir-Sb phase diagram determined in this study looks similar to analogous phase diagram, *i.e.* Co-Sb and Rh-Sb [12, 13]. However, our determination of the phase diagram appears to be significantly different from the one established in reference [2]. In our study, the temperatures corresponding to the peritectic crystallization of IrSb₃ in the range 80 to 97 at. %Sb and determined from the cooling curves were very scattered and well below the value of 1141 °C determined from the heating curves. We attributed these effects to the nonequilibrium crystallization of the alloys upon rapid cooling. In a study of the Co-Sb phase diagram [14], similar effects were observed. A peritectic decomposition temperature of 859 °C was determined from the heating curves for the compound CoSb₃. By recording the cooling curves, the temperatures of the peritectic formation of CoSb₃ were very scattered and below the temperature of 859 °C determined from the heating curves. In the previously established Ir-Sb phase diagram [2], the authors determined the liquidus temperatures from cooling curves and their results could have been affected by similar effects as those reported in this study.

4. Conclusion

A determination of the antimony-rich part of the Ir-Sb phase diagram was carried out by DTA, MPA, XRD and metallographic analyses. The existence of three compounds was confirmed in the investigated range of composition: IrSb₃ which forms by peritectic reaction at 1141 °C, IrSb₂ which also forms peritectically at 1475 ± 30 °C and IrSb which melts congruently at 1645 ± 25 °C. IrSb₃ forms a degenerate eutectic with antimony at 621 °C.

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Figures captions

Figure 1, Antimony-rich iridium antimony phase diagram. (.) determined by DTA, (V) determined by direct observation.

Figure 2. Micrograph of an Ir-Sb alloy with 88 at. % Sb after DTA. IrSb_3 crystals (light phase) can be seen within the antimony matrix (dark phase.), Magnification, X 200.

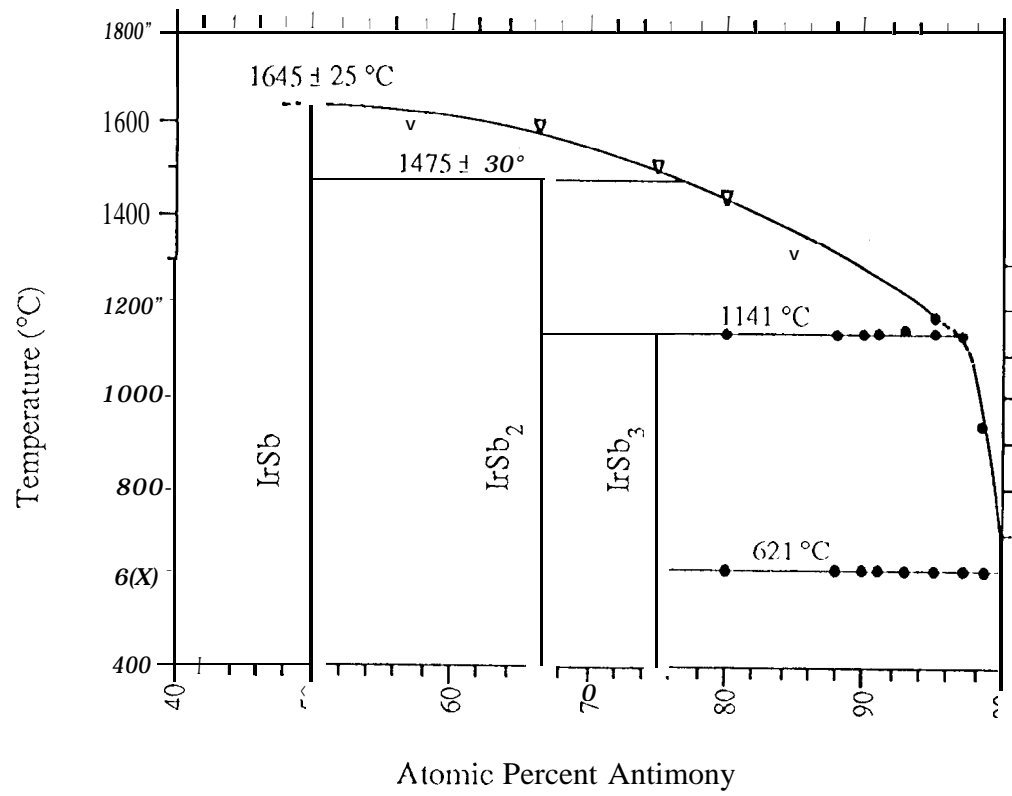
Figure 3. Micrograph of an Ir-Sb alloy with 95 at. % Sb synthesized at 1250 °C and subsequently quenched. Needle-shaped IrSb_2 crystals are seen within the antimony matrix (dark phase). Magnification, X 80.

Figure 4. Micrograph of an Ir-Sb alloy with 57 at.% Sb synthesized at 1640 °C and subsequently quenched. large IrSb crystals are seen within the IrSb_2 matrix (dark phase). Magnification, X 110.

Table1. Temperatures determined by DTA and also by direct observation (t1 and t2 from heating curves, t3 from cooling curves. The results of the determination of the different phases by MPA and XRD analyses in several iridium antimonide alloys are also reported.

(at. % Sb)	Temperatures determined by DTA (°C)		Temperatures determined by direct observation (°C)	Results of MPA and XRD after DTA	Results of MPA and XRD after quenching	
	t1	t2				
100	-	-	-	Sb	-	-
98.5	622.9	937	-	Sb + IrSb3	Sb + IrSb3	-
97	622.7	-	-	Sb + IrSb3	-	-
95	622.8	1141	-	Sb + IrSb3	Sb + IrSb2	-
93	620.7	1143	-	Sb + IrSb3	-	-
91	620.1	1147	-	Sb + IrSb3	Sb + IrSb2	-
90	622.35	1141	-	Sb + IrSb3	-	-
88	620.1	1142	-	Sb + IrSb3	-	-
85	-	1144	-	Sb + IrSb3	-	-
80	618	-	1325	Sb + IrSb3	-	Sb + IrSb2
75	-	1139	1445	Sb + IrSb3	Sb + IrSb2	Sb + IrSb2
66.66	-	1144	1505	-	Sb + IrSb2	Sb + IrSb2 + IrSb
57	-	-	1590	-	-	IrSb2 + IrSb
50	-	-	1595	-	-	IrSb2 + IrSb
			1644			IrSb

Figure 1.



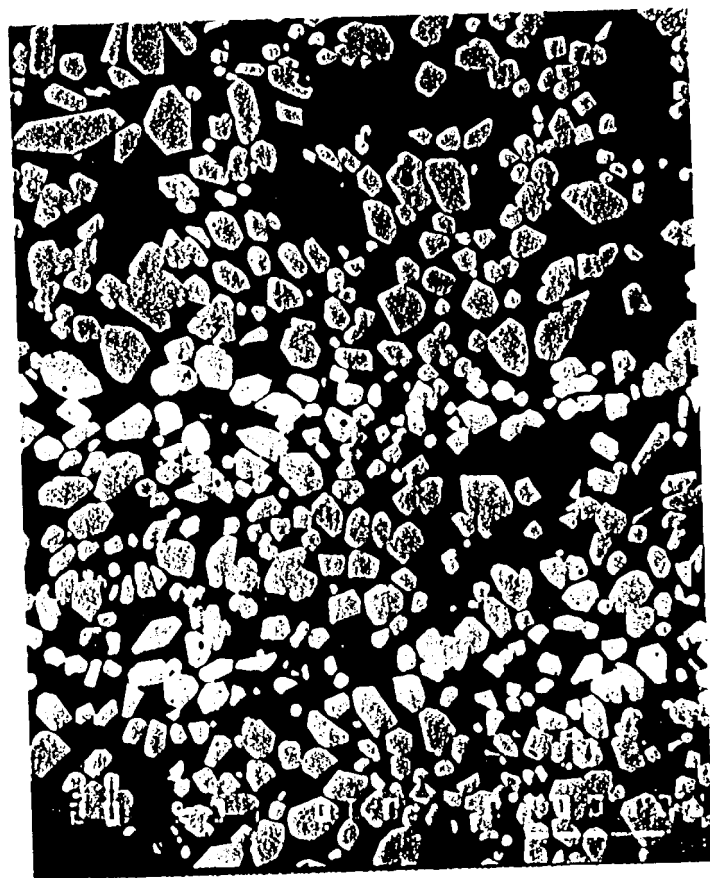


Figure 2

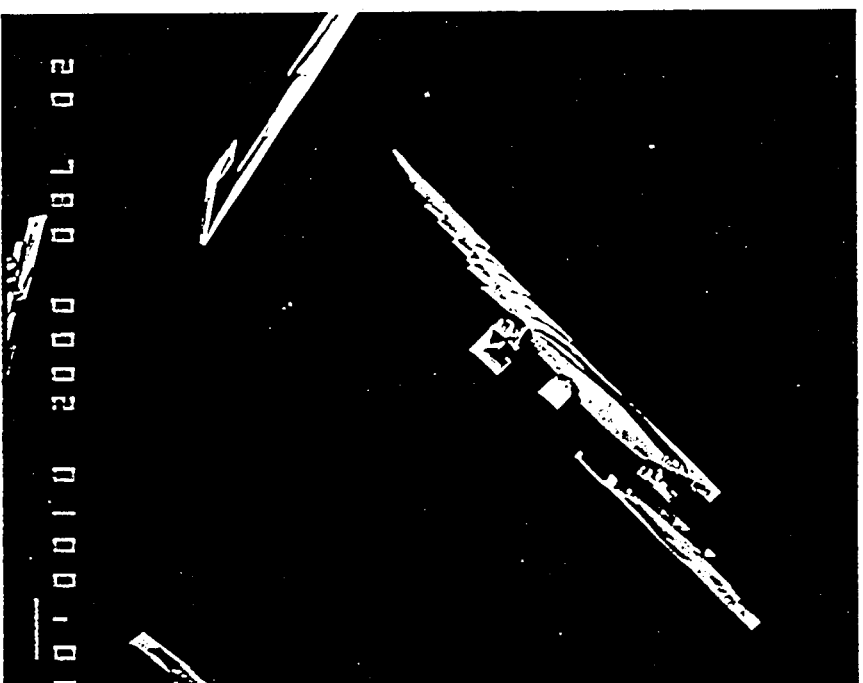


Figure 3



Figure 4